

# **SULPHUR CREEK TOTAL MAXIMUM DAILY LOAD FOR MERCURY PROBLEM STATEMENT**

## **1 INTRODUCTION**

The Federal Clean Water Act (CWA) requires states to identify impaired water bodies and to develop programs to correct the impairments. States refer to the correction program as a “Total Maximum Daily Load” (TMDL) program. This refers to the total maximum daily load of a pollutant that a water body can assimilate without impairments. In order to meet state and federal requirements, TMDLs must include several key elements including, but not limited to, the following: description of the problem, numerical water quality target, analysis of current loads and load reductions needed to eliminate impairments, plan and program of implementation to achieve the needed load reductions, and monitoring to document program progress.

The Central Valley Regional Water Quality Control Board (Regional Board) has determined that Sulphur Creek, located in Lake County is impaired because the water in Sulphur Creek exceeds the California Toxics Rule water quality objectives. In addition, macroinvertebrates have elevated mercury levels. The primary purpose of this report is to present the Problem Statement, which is the first element of the TMDL. The Problem Statement presents information that explains the overall regulatory framework for this TMDL and provides context for the problem, which is the impairment of Sulphur Creek by mercury. Regional Board staff will complete the other elements of the TMDL in accordance with the schedule included in this report.

To meet these objectives, the Problem Statement has six sections:

1. Regulatory Background and TMDL Schedule.
2. Watershed Characteristics and TMDL Scope.
3. Mercury Sources and Effects.
4. Beneficial Uses and Applicable Standards.
5. Available Monitoring Data.
6. References

## **2 REGULATORY BACKGROUND**

### **2.1 Clean Water Act 303(d) Listing and Total Maximum Daily Load Development**

Section 303(d) of the Federal Clean Water Act requires states to:

1. Identify those waters not attaining water quality standards (referred to as the “303(d) list”).
2. Set priorities for addressing the identified pollution problems.
3. Establish a “Total Maximum Daily Load” for each identified waterbody and pollutant to attain water quality standards.

The 303(d) list for the Central Valley is prepared by the Regional Board and approved by the State Water Resources Control Board (State Board) and the United States Environmental Protection Agency (USEPA). Waterbodies on the 303(d) list are not expected to meet water quality objectives even if dischargers of point sources comply with their current discharge permit requirements. A TMDL represents the maximum load (usually expressed as a rate, such as kilograms per day [kg/day]) of a pollutant that a waterbody can receive and still meet water quality objectives. A TMDL describes the reductions needed to meet water quality objectives and allocates those reductions among the sources in the watershed. Elements of a TMDL include:

- problem statement;
- numerical water quality target;
- identification and quantification of sources and source loads;
- maximum load of the contaminant that will not adversely impact beneficial uses;
- mathematical linkage between the water quality target and amount of contaminant (a linkage analysis is used to determine the amount by which current pollutant levels must be reduced in order to achieve the maximum load);
- allocation of portions of the necessary load reduction to the various sources; and
- margin of safety that takes into account uncertainties and consideration of seasonal variations.

A problem statement provides the context and background for the TMDL (USEPA, 2000a) by identifying the waterbody segments and pollutants being addressed by the TMDL, selecting the relevant water quality standards, describing the basis for the 303(d) listing, and providing an overview watershed characteristics. To establish water quality objectives under Porter-Cologne, Regional Board staff must consider the environmental characteristics of the watershed. Therefore, the problem statement should include a

description of characteristics such as land use, precipitation and runoff patterns, soil type, and hydromodification.

## **2.2 Porter-Cologne Basin Plan Amendment Process**

In general, the Regional Board will develop a water quality management strategy for each waterbody and pollutant in the Central Valley identified on California's 303(d) List. The management strategy will include several phases:

- TMDL Development: involves the technical analysis of the sources of pollutant, the fate and transport of those pollutants, the numeric target(s), and the amount of pollutant reduction that is necessary to attain the target.
- Implementation Planning: involves an evaluation of the practices and technology that can be applied to meet the necessary load reductions, the identification of potentially responsible parties, a description of the implementation framework (e.g., incentive-based, waste discharge requirements, and prohibitions), a time schedule for meeting the target(s), and a consideration of cost.
- Basin Planning: focuses on the development of a Basin Plan Amendment and a Functionally Equivalent Document for Regional Board consideration. The Basin Plan Amendment will include those policies and regulations that the Regional Board believes are necessary to attain water quality objectives. The Functionally Equivalent Document includes information and analyses required to comply with the California Environmental Quality Act.
- Implementation: focuses on the establishment of a framework that ensures that appropriate practices or technologies are implemented (§13241 and §13242 of the Porter-Cologne Water Quality Act), including those elements necessary to meet federal TMDL requirements (CWA Section 303(d)).

The Basin Plan Amendment is legally applicable once the Regional Board, State Board, Office of Administrative Law, and the USEPA approve it.

## **2.3 Timeline and Process for the Sulphur Creek Mercury Management Strategy**

Regional Board staff are currently working on the TMDL Development phase of the Sulphur Creek mercury management strategy. Public input on implementation planning options would provide support for modifying the recommendations in the TMDL Report. A Basin Plan amendment would be developed to implement the TMDL. The Basin Plan Amendment would contain any modifications to the TMDL Report, along with the accompanying Functionally Equivalent Document and staff report, which Regional Board staff will present to the Regional Board for adoption. Regional Board staff may prepare a Use Attainability Analysis as part of the Basin Plan Amendment should an evaluation of implementation options indicate that Sulphur Creek beneficial uses could not be reasonably attained.

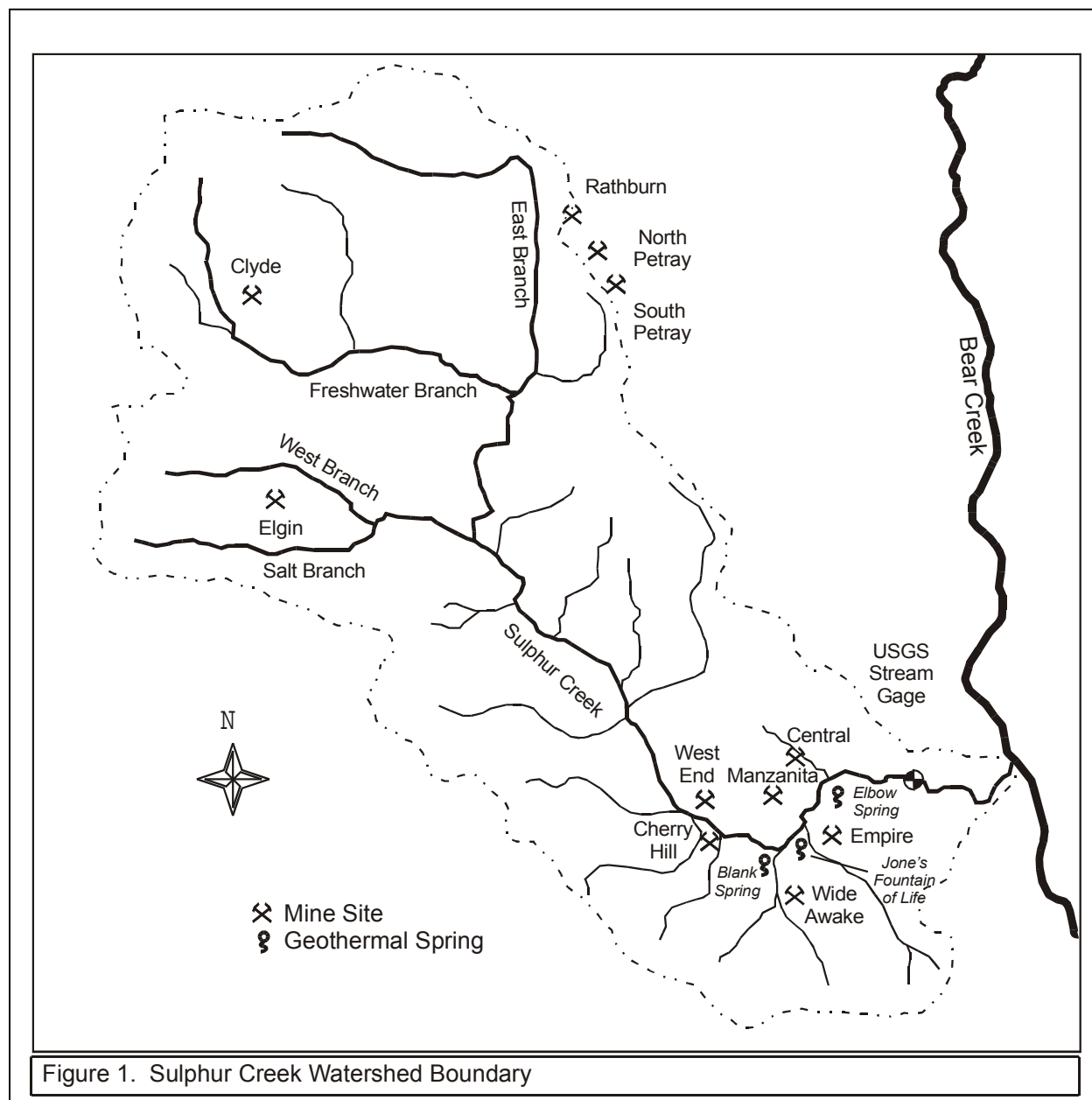
Regional Board Staff intend to seek public input throughout the TMDL Development and Implementation Planning phases. As Regional Board Staff develops documents related to preparation of the Basin Plan Amendment, formal public workshops and hearings will be held.

### **3 WATERSHED CHARACTERISTICS AND TMDL SCOPE**

Sulphur Creek drains a 6543-acre watershed in the Coast Range of California (Figure 1). The scope of the TMDL encompasses the 7-mile reach from the headwaters of Sulphur Creek to its confluence with Bear Creek, approximately twelve miles upstream from the Bear Creek-Cache Creek confluence (SWRCB, 1999; USGS, 1991). Sulphur Creek is an ephemeral stream that flows between the fall and spring months (October through June) (USGS, 2001). Watershed land use is predominantly rangeland in undeveloped chaparral and California scrub oak (Foe and Croyle, 1998).

The nearest rain gage to Sulphur Creek is at the Indian Valley Reservoir. Precipitation at the reservoir between the 1996 and 2001 water years typically averaged 25 inches per year; however, precipitation exceeded 45 inches in an above-average wet year. The majority of rain typically falls between November and March. During the winter, snow occasionally falls in the mountains above the 3,000-foot elevation. Mean annual temperatures for the region are approximately 62 degrees Fahrenheit (°F), with summer temperatures exceeding 100°F and winter temperatures dropping below freezing.

Sulphur Creek is within the Cache Creek watershed. The upper portion of the watershed begins in the Clear Lake basin, which is in the northern Coast Range geomorphic province, approximately 60 miles east of the San Andreas Fault. The Clear Lake basin is a fault-bounded subsiding depression, believed to be a pull-apart basin related to a releasing bend in the San Andreas Fault. The regional bedrock of the Coast Range consists of a structurally complex group of rocks known as the Franciscan Formation, which formed during the Late Jurassic to Cretaceous period when sediments on the sea floor were scraped off and piled onto the continent as the Pacific plate was subducted beneath the North American Continental plate. Regional volcanic activity since that time may be related to the extensional faulting in the Clear Lake basin. The shallow magma chamber beneath the Geysers-Clear Lake area is the source of geothermal activity throughout the region. The U.S. Geological Survey (USGS) has mapped numerous



hot springs discharging in the area. A large number of these geothermal springs flow directly into drainages in the Cache Creek watershed including Sulphur Creek.

## **4 MERCURY SOURCES AND EFFECTS**

### **4.1 Mercury Sources in the Sulphur Creek Watershed**

The Sulphur Creek watershed is in the Coast Ranges, a region naturally enriched in mercury. Active geothermal vents and hot springs deposit mercury, sulfur, and other minerals at or near the earth's surface. Most of the mercury deposits in California occur within a portion of the Coast Ranges geomorphic provinces extending from Clear Lake in the north to Santa Barbara County in the south. Approximately 90% of the mercury (roughly 104 million kilograms) used in the United States between 1850 and 1988 was mined in the Coast Ranges of California. Much of the mining and extraction occurred before 1890 when mercury processing was crude and inefficient. Researchers estimate that approximately 34.5 million kilograms of mercury was lost to the environment from historic mercury mining activity (Churchill, 2000). As a result, high levels of mercury are present in some streams, lakes, and reservoirs in the Coast Range, in the Sacramento River, and in the Sacramento – San Joaquin River Delta.

Sources of mercury entering Sulphur Creek include geothermal springs, rangeland runoff, erosion of naturally mercury-enriched soils and excavated overburden and tailings from historic mining operations, and atmospheric deposition. The majority of mercury in Sulphur Creek comes from the Sulphur Creek Mining District (Foe and Croyle, 1998). The mining district includes six inactive mines (Central, Empire, Wide Awake, Cherry Hill, West End and Manzanita) in the lower watershed and five inactive (Clyde, Elgin, Rathburn, South Petray and North Petray) mines in the upper watershed.

Regional Board staff determined that the largest mercury loads were exported from the upper basin of Cache Creek after storms (Foe and Croyle, 1998). To identify the major sources of mercury in the upper basin, staff conducted three surveys during storm flow events between January 1997 and February 1998 (Foe and Croyle, 1998). Three surveys took place in Bear Creek. Staff collected water samples from the mouth of Sulphur Creek and from locations up and downstream of the tributary input to ascertain whether the tributary enhanced or diluted mercury concentrations in Bear Creek. During two surveys, mercury concentrations in Sulphur Creek were high enough to increase downstream concentrations in Bear Creek

four to six fold. Water samples collected from Sulphur Creek had mercury levels ranging between 1,964.7 and 8,401.7 ng/L.

#### 4.2 Mercury Chemistry and Accumulation in Biota

Mercury (Hg) can exist in various forms in the environment. Physically, mercury may be present in air as mercury vapor, dissolved in the water column, or associated with solid particles in air, water, or soil.

Chemically, mercury can exist in three oxidation states: elemental ( $\text{Hg}^0$ ), mercurous ion (monovalent,  $\text{Hg}^+$ ), or mercuric ion (divalent,  $\text{Hg}^{+2}$ ). Ionic mercury can react with other chemicals to form both organic and inorganic compounds and can be converted by sulfate reducing bacteria to more toxic organic compounds, such as methylmercury or dimethylmercury. Important factors controlling the conversion rate of inorganic to organic mercury include temperature, percent organic matter, redox potential, salinity, pH, and mercury concentration. Neither the primary locations of methylmercury production nor the principal factors controlling methylation are yet known for any location in the Central Valley.

Both inorganic mercury and organic mercury can be taken up from water, sediments, and food by aquatic organisms. Because organic mercury uptake rates are generally much greater than rates of elimination, methylmercury concentrates within organisms.

Low trophic level<sup>1</sup> species such as phytoplankton obtain most mercury directly from the water.

*Bioconcentration* describes the net accumulation of mercury directly from water. The *bioconcentration factor* is the ratio of mercury concentration in an organism to mercury concentration in water. However, predatory species such as piscivorous (fish-eating) fish and birds obtain most mercury from mercury-containing prey rather than directly from the water (USEPA, 1997b). A *bioaccumulation factor* describes the degree to which mercury accumulates from water and prey, relative to mercury concentration in the water. Compounds *bioaccumulate* when rates of uptake are greater than rates of elimination.

Repeated consumption and accumulation of mercury from contaminated food sources results in tissue concentrations of mercury that are higher in each successive level of the food chain. This process is termed *biomagnification*. Methylmercury readily accumulates in fish due to efficient uptake from dietary

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<sup>1</sup> Trophic levels are the hierarchical strata of a food web characterized by organisms that are the same number of steps removed from the primary producers. The USEPA's 1997 Mercury Study Report to Congress used the following criteria to designate trophic levels based on an organism's feeding habits:

Trophic level 1: Phytoplankton.

Trophic level 2: Zooplankton and benthic invertebrates.

Trophic level 3: Organisms that consume zooplankton, benthic invertebrates, and phytoplankton.

Trophic level 4: Organisms that consume trophic level 3 organisms.

sources and low rates of elimination. The proportion of total mercury that exists as the methylated form generally increases with level of the food chain, approaching greater than 90% in top trophic level fish (Nichols et al., 1999). This occurs because inorganic mercury is less well absorbed and/or more readily eliminated than methylmercury. Field studies indicate that diet is the primary route of mercury uptake by fish (Wiener and Spry, 1996). Methylmercury is the predominant form of organic mercury present in biological systems. Dimethylmercury, which is an unstable compound that dissociates to methylmercury at neutral or acid pH, is not considered a concern in freshwater systems (USEPA, 1997a).

Diet is the primary route of methylmercury exposure for organisms that consume fish and aquatic invertebrates. Although a few studies have indicated that methylmercury impairs reproduction of some fish (Huber, 1997; Wiener and Spry, 1996), the greatest concern for mercury toxicity is in higher trophic-level organisms that consume aquatic life. The aquatic food web provides more than 95% of humans' intake of methylmercury (USEPA, 1997a).

### **4.3 Toxicity of Mercury**

#### **4.3.1 Effects on Humans**

Mercury is a potent neurotoxin in humans. Developing fetuses and young children are at greatest risk of toxicity from mercury (NRC, 2000). Although the inhalation of elemental mercury fumes can cause harm, exposure to levels of concern most frequently occurs through the consumption of methylmercury in fish tissue. Researchers have documented the toxicity of mercury to humans in populations consuming contaminated fish (Davidson et al., 1998; Grandjean et al., 1997; Tsubaki and Irukayama, 1977) and grains treated with methylmercury-containing fungicide (Bakir et al., 1973). Consumption of highly contaminated fish caused multiple effects, including tingling or loss of tactile sensation (paresthesia<sup>2</sup>), loss of muscle control, blindness, paralysis, birth defects, and death. Children whose mothers ate fish during pregnancy may be at risk for more subtle behavioral and neurodevelopmental impairments (Crump et al., 1998; Davidson et al., 1998; NRC, 2000). Researchers also determined that children who eat fish themselves are more sensitive to mercury than adults because their neural systems are still developing and they tend to consume more fish per body weight than adults (Grandjean et al., 1999; Mahaffey, 1999). Effects in children exposed early in development appear at dose levels five to ten times lower than dose levels associated with toxicity in adults (NRC, 2000).

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<sup>2</sup> Paresthesia is an abnormal "prickling" sensation in the skin and is an early clinical symptom of neurological damage.



Although the largest body of literature addresses effects of mercury on neurodevelopment, studies have found impairment of other human organ systems as well. Exposure to mercury causes reduced fertility, adverse cardiovascular effects, immunotoxicity, and alters cell division (NRC, 2000; Speirs and Speirs, 1998).

Effects of mercury are dependent upon the dose received. There is no current evidence of acute or chronic mercury toxicity to humans due to consumption of fish from Clear Lake or Cache Creek. However, researchers have not yet conducted extensive fish consumption and effect studies in the region. Existing fish consumption advisories for Clear Lake, presented in terms of pounds of fish that humans can safely consume, are based upon the risk for average adult consumers of developing a non-fatal, neurologic impairment of paresthesia (Stratton et al., 1987).

#### ***4.3.2 Effects on Wildlife***

Wildlife species also exhibit detrimental effects from mercury exposure. Researchers have observed behavioral effects – such as impaired learning, reduced social behavior and impaired physical abilities – in mice, otter, mink and a primate species (crab-eating macaques) exposed to methylmercury (Wolfe et al., 1998). Researchers have also observed reproductive impairment following mercury exposure in multiple species, including common loons and western grebe (Wolfe et al., 1998), walleye (Huber, 1997), and mink (Dansereau et al., 1999).

## **5 BENEFICIAL USES AND APPLICABLE STANDARDS**

### **5.1 Sulphur Creek Beneficial Uses**

Both the Federal Clean Water Act and the State Water Code (Porter-Cologne Water Quality Act) require identification and protection of beneficial uses. The beneficial uses designated in Table II-1 of the Water Quality Control Plan (Basin Plan) for the Sacramento and San Joaquin Basins (CVRWQCB, 1998) are intended to meet all applicable State and Federal requirements. Beneficial uses for Sulphur Creek are not explicitly assigned in the Basin Plan, however the Basin Plan states that the beneficial uses of any specifically identified water body generally applies to its tributary streams. Sulphur Creek is a tributary to Bear Creek, which is a tributary to Cache Creek. Table 1 lists the existing and potential beneficial uses of Cache Creek as they apply to Sulphur Creek.

Table 1. Existing and Potential Beneficial Uses of Sulphur Creek (CVRWQCB, 1998)

Beneficial Use	Status
Municipal and domestic supply (MUN)	existing
Agriculture – irrigation and stock watering (AGR)	existing
Industry – process (PROC) and service supply (IND)	existing
Recreation – contact, canoeing, and rafting (REC-1) and other non-contact (REC-2)	existing
Freshwater habitat (Warm)	existing
Freshwater habitat (Cold)	potential
Spawning (SPWN) – warm and cold	existing
Wildlife habitat (WILD)	existing

## 5.2 Water Quality Objectives

The narrative water quality objective for toxicity in the Basin Plan states, in part, “All waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life.” The narrative toxicity objective further states that “The Regional Water Board will also consider ... numerical criteria and guidelines for toxic substances developed by the State Water Board, the California Office of Environmental Health Hazard Assessment, the California Department of Health Services, the U.S. Food and Drug Administration, the National Academy of Sciences, the USEPA, and other appropriate organizations to evaluate compliance with this objective.” (CVRWQCB, 1998)

The USEPA and the California Department of Health Services determined a primary maximum contaminant level (MCL) of 2.0 micrograms per liter ( $\mu\text{g/L}$ ) (2,000 ng/L) of mercury for drinking water (Marshack, 2000). The USEPA established a recommended ambient water quality criterion of 1.4  $\mu\text{g/L}$  (1,400 ng/L) total mercury (maximum concentration, 1-hour average) and 0.77  $\mu\text{g/L}$  (770 ng/L) total mercury (continuous concentration, 4-day average) for the protection of freshwater aquatic wildlife (USEPA, 1999). In addition, the USEPA promulgated the California Toxic Rule (CTR) in April 2000 (USEPA, 2000b). The CTR contains a water quality objective of 0.05  $\mu\text{g/L}$  (50 ng/L) total recoverable mercury for freshwater sources of drinking water. The CTR criterion protects humans from exposure to mercury in drinking water and contaminated fish. The standard is enforceable for all waters with a municipal and domestic water supply and/or any aquatic beneficial use designation. Harley Gulch has such a beneficial use designation. The federal rule did not specify duration or frequency terms; however, researchers have previously employed a 30-day averaging interval with an allowable exceedance frequency of once every three years for protection of human health,

which is recommended for this effort (Marshack, personal communication). The United States Fish and Wildlife Service (USFWS) and the National Marine Fisheries Service (NMFS) were concerned that the USEPA's mercury objective in the CTR would not be sufficiently protective of threatened and endangered species. The USEPA has committed to revising its water quality objective to include protection of wildlife. The final water quality value for wildlife protection is not yet known.

Mercury concentrations in Sulphur Creek frequently exceed water quality objectives for protection of drinking water, as adopted in the California Toxics Rule. In addition, mercury transported from Sulphur Creek downstream to Bear Creek and Cache Creek poses a risk in these areas. Cache Creek is a major source of mercury to the Sacramento-San Joaquin Delta Estuary. Monitoring has demonstrated that in wet years Cache Creek may contribute half of all the mercury transported into the Estuary. Recent work has shown that aquatic organisms downstream of Sulphur Creek have elevated concentrations of mercury. The mercury TMDL control program for Sulphur Creek must also consider actions needed to protect downstream beneficial uses in Bear Creek.

## **6 AVAILABLE MONITORING DATA**

Benthic invertebrate and water data indicate that Sulphur Creek is impaired by mercury. The sections below summarize the available environmental data and describe the extent of mercury impairment.

### **6.1 Benthic Aquatic Invertebrates**

In the spring of 1996, researchers collected benthic invertebrate samples in the upper Bear Creek basin to determine mercury bioavailability (Slotton et al., 1997b). In addition, as part of the ongoing CALFED mercury grant, UC Davis researchers collected benthic invertebrate samples in February, May, and August 2000 to determine whether there is a relationship between aqueous mercury and biotic concentrations (Slotton et al., 2001). The methods for both sampling efforts were analogous to those used in the Sierra Nevada Mountains (Slotton et al., 1997a). Sulphur Creek invertebrate samples had some of the highest concentrations of mercury associated with the Cache Creek watershed and mercury concentrations were much higher than any observed in comparable samples from the Sierra Nevada Mountains. Concentrations ranged from 1.17 to 2.69 micrograms per gram (ug/g) (parts per million [ppm]). The highly localized nature of the contamination was demonstrated by the lower mercury concentrations measured in invertebrates from adjacent streams

without mercury mining. Invertebrate mercury concentrations decreased with increasing distance from mine areas.

The benthic invertebrate studies also suggested that, although Sulphur Creek invertebrate mercury concentrations are high, much of the large bulk mercury loads observed in Foe and Croyle's 1998 study may not be easily methylated by sulfate-reducing bacteria.

## 6.2 Water Data

Limited water column mercury information exists for Sulphur Creek (Foe and Croyle, 1998). Regional Board staff collected water samples from the mouth of Sulphur Creek during storm runoff events in the winter season (November through March) between January 1997 and February 1998 (Foe and Croyle, 1998). Table 2 lists the percentage of samples that had mercury concentrations exceeding the CTR criterion (50 ng/L).

Table 2. Summary of Exceedances of Mercury Criteria in Sulphur Creek Water Samples  
(Source: Foe & Croyle, 1998)

Sampling Location (upstream to downstream)	# of Samples <sup>(a)</sup>	Concentration Ranges (ng/L)	Percentage of Samples Exceeding CTR Criterion (50 ng/L)
Sulphur Creek before the confluence with Bear Creek	2	1,964.7 - 8,401.7 (1,142.1) <sup>b</sup>	100 %

(a) Samples were collected during storm periods.

(b) Field duplicate

Regional Board staff determined that storm runoff events accounted for the majority of the mercury exported from Sulphur Creek. Researchers are currently collecting information as part of the ongoing CALFED mercury grant to better define mercury concentrations in Sulphur Creek.

## 6.3 Mercury Loading Patterns

Regional Board Staff completed a mercury loading study for the Sacramento-San Joaquin Delta Estuary that determined Sulphur Creek was a major source of mercury to Bear Creek. Staff undertook synoptic

surveys in the Sulphur Creek watershed during two hydrologic cycles between February 1996 and February 1998 (characterized by wet winters) to attempt to characterize mercury concentrations and loads and to identify sources (Foe and Croyle, 1998). Staff identified winter storm-runoff as the main mercury-loading pattern in Sulphur Creek.

The storm-runoff pattern was observed during and immediately after large storms, when sufficient rain had fallen to saturate the soil profile and induce sheet runoff. Storm-runoff periods occur with a frequency of four to ten times per year. Overall, infrequent storm runoff events appeared to account for the majority of the mercury exported from the basin.

As part of the ongoing CALFED mercury grant, the USGS is measuring methyl and total mercury concentrations in Sulphur Creek to determine:

- the efficiency with which methyl mercury is being produced;
- the relationship between total mercury concentrations and efficiency of methyl mercury generation from sediment; and
- the total loads of mercury being transported in the drainage.

The USGS constructed a gage station on Sulphur Creek and is completing additional loading estimates in the basin. In addition, UC Davis is conducting detailed studies at the mine sites in Sulphur Creek to determine the precise locations responsible for off-site mercury movement.

## **6.4 Summary**

Available data indicate that elevated levels of mercury exist in water and macroinvertebrates in the Sulphur Creek watershed. The Regional Board added Sulphur Creek to the 303(d) list in 1998 due to elevated mercury levels in water and benthic invertebrates.

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